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QUARTERLY REPORT

GTI PROJECT NUMBER 20916

Modeling of Microbial Induced Corrosion on Metallic Pipelines Resulting from Biomethane and the Integrity Impact of Biomethane on Non-Metallic Pipelines

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Project Objective

The objective of this project is to understand key elements related to promoting the successful delivery of biomethane into natural gas pipeline networks. This project focuses on two key areas of concern: [1] the effect of microbial induced corrosion on metallic pipes and [2] the impacts of biogas/biomethane on a non-metallic gathering network from sustained biogas feedstock exposure. This report summarizes the work that has been conducted through the first quarter of 2011. Results from Tasks 3 and 8 are discussed in detail within this report.

List Activities/Deliverables Completed During Reporting Period

		SCH Date	CMPL Date
Task #3	Lab Evaluation of Microbial Corrosion	03/31/2011	In Progress

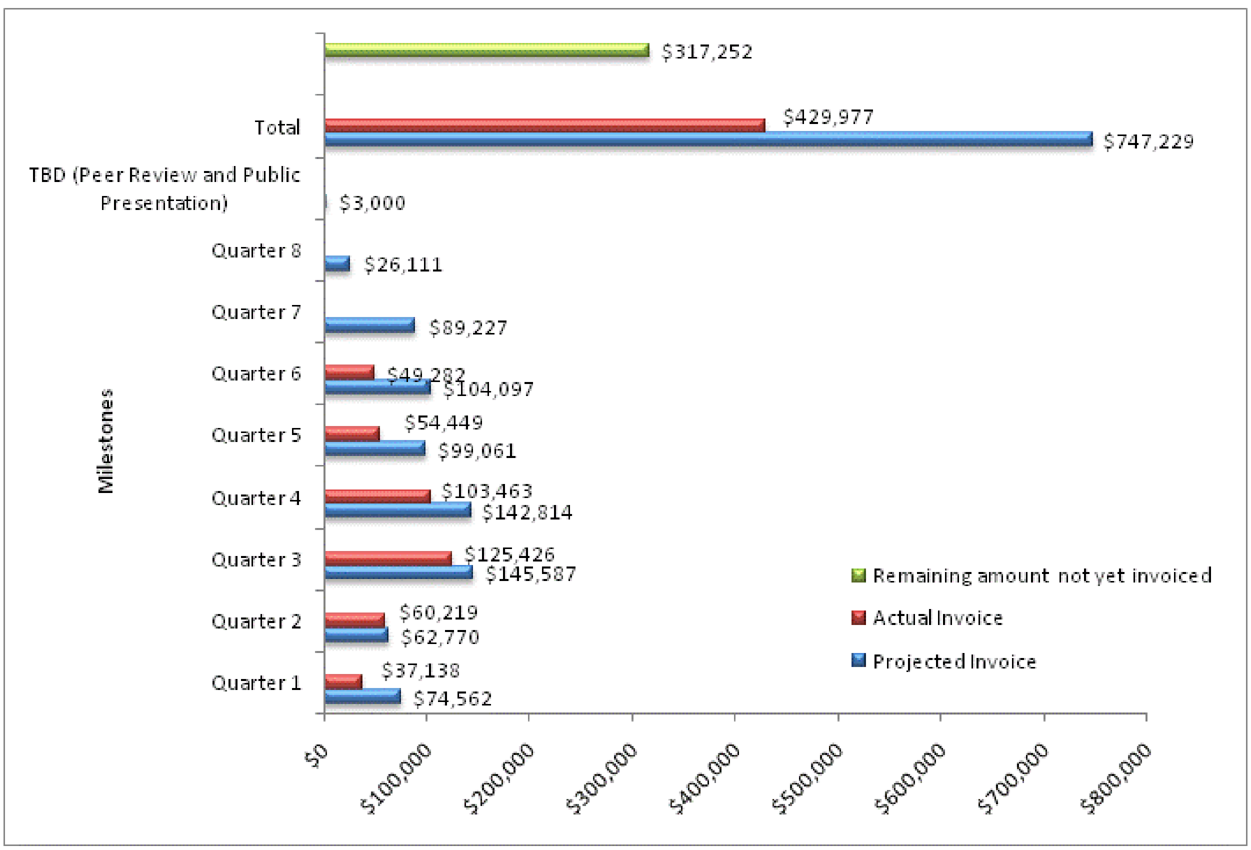
- Continued work on electrochemical cell and troubleshooting sterility issues

		SCH Date	CMPL Date
Task #8:	Perform Bounded Testing	6/30/2011	In Progress

- Revised biogas collection protocol.
- Revised pressure test vessel and completed construction of saturation test setup.
- Obtained plastic pipe and elastomer test materials.
- Obtained natural gas sample and performed chemical composition analysis.
- Performed baseline material property testing.

Funds and Work Completed During this Quarterly Period

Figure 1. Quarterly Payable Milestones/Invoices - DTPH56-09-T-000002



Technical Status

Task 3 - Lab Evaluation of Microbial Corrosion under Simulated Field Conditions

Conditions for Modeling Experiments

We encountered some unexpected technical challenges in this quarter. The biggest challenge in Task 3 was an issue of sterility. The bacteria in one cell are finding a way to migrate to another cell, which is supposed to be kept sterile during the experiment. Many methods and procedures to sterilize and assemble the unit were tested, modified, and re-tested. So far we were able to narrow the problem down to a few possible contamination reasons, but we still need more time to fully resolve this issue. Execution of Task 4 is dependent on the data collected in Task 3 and we must resolve this issue first before we can collect the modeling data for Task 4.

We have tested different sterilization methods including sonication, wet autoclave, dry autoclave, UV, SSDS (a sporicidal agent), acetone, and various combinations, and different components in the cells were sterilized in different ways due to the properties of the components. We also tested different methods to assemble the cells after sterilization with an attempt to minimize the assembly steps post sterilization. We verified each sterilization step and cell components assembly, and found that both cells were able to maintain sterile conditions before bacteria inoculation. However, after inoculation of the anode cell, the cathode cell continued to show bacteria growth after a few days. Bacteria in the anode cell somehow manage to migrate into the cathode cell through the bridge tube that is equipped with a membrane filter.

The filter tests include filters from different manufacturers with pore sizes ranging from 0.1 to 0.45 µm. The way the filters were installed in bridge tube between two cells was also studied. Unfortunately all tests performed in the two-cell system failed to keep one cell sterile after bacteria inoculation in another cell. Filter failure can be caused by various reasons, such as filter damage during sterilization, filter defects, or medium circulation in anode cell which may generate some pressure on the filter and result in failure.
An experiment was performed to compare five pre-sterile filters from different vendors. One flask was inoculated with bacteria and connected to another flask with no inoculation. The connection tube was equipped with various filters. The flasks were incubated at 30°C for two weeks, without agitation, in a slightly inverted position to prevent air pockets in the silicon tubing from forming. The medium uninoculated flasks with Gelman Acrodisc PTFE 0.45 µm filter and Millipore Millex-VV PVDF 0.1 µm filter maintained clear after a two-week incubation period, though the precipitation started to show up after 6 and 10 days, respectively. The medium in uninoculated flasks with Pall Acropak 1000 Supor membrane 0.8/0.2µm filter also maintained clear after a two-week incubation period, though the mold growth was visible after 12 days. We will confirm by streak plating if there is bacteria growth in uninoculated flasks from the above three setups. We will also confirm if the contact between the rubber stopper and medium is the cause of precipitation seen in the uninoculated flasks. Note: rubber stopper will not have contact with medium in a real two-cell system.

After the proper filter is identified in the confirmation experiment, and then further confirmed in two-cell system, we will be able to setup the experiments in a two-cell system and collect the required modeling data.

Task 8 - Perform Bounded Testing to Generate a Strong Example Data Set

The activities of Task 8 in this quarter include (a) revising the protocol for collecting the raw/processed biogas samples from the plants, (b) revising and building saturation test setup, (c) obtaining plastic pipe and elastomer materials for testing, (d) obtaining natural gas sample and performing chemical composition analysis, and (e) preparing test materials and performing baseline testing.

Revision has been made on the biogas collection protocol based on the comments from baseline hazard analysis. In addition, the site for collecting landfill raw and processed gases was changed due to the need for a larger size outlet pipe on the biogas reactor to provide enough flow for the compressor.

Modifications have been made on the gas saturation test setup with an additional small pressure vessel added into the system for placing the head space test samples which will be used for measuring saturation curve. The benefit of adding this separate pressure vessel is that it will maintain the main vessel under test temperature and pressure when the headspace test samples are periodically retrieved for analysis.

Commercial pipe-grade Medium Density Polyethylene (MDPE) PE 2708 resin was obtained. Plaques were molded using this resin and will be machined into the test samples. Acrylonitrile Butadiene Rubber (NBR) and Styrene Butadiene Rubber (SBR) sheet materials were obtained to make test samples. The formulations and properties of the selected NBR and SBR sheet materials are similar to the rubber materials used in natural gas pipeline system. Several baseline tests were performed on the rubber sheet material to verify the material properties.

Natural gas sample has been obtained for use as reference gas. It reflects a gas quality typical to tariffs imposed by LDCs located in the Midwest. Full chemical analysis was performed to determine actual compositions.

Protocol for Biogas Collection

Revised Biogas Collection Protocol

A piping and instrumentation diagram (PID) drawing was made for the sampling process. Improvements were made to the original configuration by adding a bypass to the desiccant line for the dry processed gas collection. Additional pressure relief valves were added based on a Hazardous Operations (HAZOP) assessment. The updated PID is shown in Figure 2; and materials and equipment that GTI currently has in hand are denoted with a green tag.

Biogas/Biomethane Gas Sample Sites

The biogas/biomethane gas sample sites have been selected. These include a landfill site for raw and processed landfill gas samples and a dairy farm site for raw dairy gas. The compositions of the biogas/biomethane gases from these sites are representative to the gases that have been analyzed at GTI.

Gas Saturation Test Setup

The test samples will be saturated in the sample gases including one natural gas (reference), one raw landfill gas, one processed landfill gas (biomethane) and one raw dairy gas. The gas saturation will be performed at ~ 45ºC to simulate a "worse case scenario" of a biogas gathering line where biogas is delivered right out of the digester.

The modified gas saturation test setup is shown in Figure 3, and consists of a main pressure vessel and a second small pressure vessel. A shut off valve is installed in-between the main and second pressure vessel. The main pressure vessel is used for housing all the comparative test samples. The second pressure vessel is for the head space test samples that will be used to generate the gas saturation curve. When the head space samples are periodically retrieved for analysis (during the saturation test), the shut off valve will be closed so that the test samples in the main vessel will be maintained at the test temperature and pressure without interruption. The vessels will be purged with the tested gas before the test is started. Reduced gas flow will be maintained during the saturation test (0.05 ml/min).

The main pressure test vessel is constructed from a three-foot long, four inch diameter stainless steel (SS316) pipe. The pipe will be heated with heat tape wrapped around its outer surface. The temperature inside the pipe will be maintained at 45±5ºC by a temperature controlling system. The test samples will be loaded onto a sample cage made of stainless steel meshes to fully expose them to the gas. The main pressure vessel and the sample cage are shown in Figure 4.

The second vessel is made and modified from a stainless steel pipe end cap and fitting, see Figure 5. A three-layer sample cage made of stainless steel mesh will be used to hold the test samples. The gas inlet tube extends into the bottom of the vessel to ensure the gas flow pass through the test samples before it vents out of the top of the vessel. The temperature of the vessel will be monitored using a thermal couple located in its center. The vessel will be heated with heating strip wrapped around the vessel and the temperature inside the vessel will be maintained at 45±5ºC by a temperature controlling system.

Test Materials

Sheet Rubber (NBR and SBR) Materials

Sheet rubber material was decided to be used for the testing in order to prepare the samples with a standard sample size. This will reduce the data scatter resulted from sample variation and improve the comparative test results for a better evaluation of the impact from biogas/biomethane. GTI has reviewed the NBR and SBR materials that are typically used in natural gas piping systems, and selected the rubber sheet materials that have similar physical and chemical properties.

Table 1 shows the properties of the rubber sheet materials that will be used for preparing the test samples. The NBR meets the specification of ASTM D2000 (2BG715), and the SBR meets the specification of ASTM D2000 (M1AA604). The premium grad SBR sheet rubber that meets military specification (MIL-PRF-1149 Type II Class 2) was originally obtained as testing material, but the received material was out of specification and returned. Due to the required quantities and the lead time for the manufacture to make replacement of this material, GTI decided to use ASTM D2000 (M1AA604).

Pipe Grade MDPE Resin

A pipe grade (PE2708) MDPE resin was obtained to make test samples; the properties of the resin are shown in Table 2. Plaques molded with this resin will be machined into test specimens of the required dimension.

Natural Gas Sample

A "standard" natural gas was obtained for the saturation test as a reference to compare the impact from biogas/biomethane on the pipeline materials. Major components of the gas were analyzed by gas chromatography using ASTM D1945/D1946. Trace sulfur was analyzed by using ASTM D6228. Results are shown in Table 3.

Biogas/Biomethane Samples

Sites have been selected to collect processed biomethane from landfill, raw landfill biogas, and raw dairy farm biogas. Change has been made to the sampling site for collecting landfill gases (raw and processed) to meet the requirement for the outlet piping size on the biogas reactor. The approximate chemical compositions of the raw and processed biogases from the selected sampling sites are shown in Table 4. These values were obtained from GTI's database of the selected sites. A full analysis will be performed to obtain compositions of each of the gases.

Sample Preparation

Table 5 summarizes the test specimens (sizes and numbers) in one batch of gas saturation test. The rubber samples are cut from the rubber sheet material to size. The plastic test specimens are machined to size from molded plaques. The tensile specimens are prepared by die cut (ASTM D638 Type IV). The compression test samples will be die cut from the 5.7"×2.25"×0.125" plaques after the gas saturation test. To perform hardness and compression test for SBR and NBR, the specimens with 0.125" thickness will be stacked to the required sample thickness (0.25" for hardness and 0.5" for compression) according to ASTM D2240 and ASTM D575. The surface of the test specimens will be cleaned with isopropyl alcohol, rinsed with water and dried in air before loading into the saturation test chamber.

Baseline Testing

Density

The densities of the materials were analyzed using a helium pycnometer. This test method is internal to GTI (PP 300). Results from this test are listed in Table 6.

Hardness

Hardness testing was performed using a shore hardness testing apparatus. The test method being used is ASTM D2240. Results to date are shown in Table 6.

Glass Transition/Melting Point

Glass transition temperature and melting point are determined using a differential scanning calorimeter (DSC). The method used is ASTM D3418. Results to date are shown in Figure 5.

Chemical Makeup

Chemical makeup of the materials is performed using forier transform infrared spectroscopy (FTIR). The test methods are ASTM D3677 and ASTM E1252. The spectra are shown in Figures 6 through 8.

Extractable Content

Extractable content testing is only performed on the elastomers. The test method is ASTM D297. Samples are refluxed in methyl ethyl ketone (MEK) solution, and distilled to concentrate the samples. The extracts are then analyzed by FTIR. Mass loss percentages are listed in Table 6, and the extract spectra are shown in Figures 9 and 10.

Table 1. The Properties of NBR and SBR Rubber Sheet Materials

Rubber Sheet	Hardness (Shore A)	Tensile (psi)	Ultimate Elongation (%)	Heat Aging	Oil Resistance	Temperature Range (ºF)
NBR	70	1500 min	250 min	(70 hrs @ 100ºC) Hardness: ±15 points Tensile: ±30% max Elongation: -50% max	(70 hrs @ 100ºC) Hardness: -10 to +5 points Tensile: -45% max Elongation: -45% max Volume: 0 to 25% max	-40 to 200
SBR	60-70	600	200	NA	NA	-13 to 158

Table 2. The Properties of the MDPE Resin (PE2708) Selected for the Testing

Properties	Nominal Value	Test Method
Density	0.94 g/cm3	ASTM D792
Melt Index	190ºC/2.16 kg: >0.15 g/10 min	ASTM D1238
	190ºC/21.6 kg: 9.5 g/10 min	
Tensile Strength (Yield)	>2,600 psi	ASTM D638
Tensile Elongation (Break)	>600%	ASTM D638
Flexural Strength-2% Secant	>90,000 psi	ASTM D790B
Hydrostatic Strength	73ºF: 1250 psi	ASTM D2837
	140ºF: 1000 psi	
Resistance to Rapid Crack Propagation, Pc	Calculated, Full Scale (32ºF): >560 psi	ISO 13478
	S-4 (32ºF): >145 psi	ISO 13477
Resistance to Rapid Crack Propagation, Tc	S-4 @ 5 bar: <28ºF	ISO 13477
Slow Crack Growth PENT	>15000 hr	ASTM F1473
Brittleness Temperature	<-103ºF	ASTM D746A
Thermal Stability	>428ºF	ASTN D3350
Melt Temperature Range	290 ºF	ASTM D3418

Table 3. Chemical Compositions of Natural Gas Sample

Gas Property	Natural Gas
Methane (CH_4)	95.7%
Carbon Dioxide (CO_2)	0.98%
Nitrogen (N_2)	1.01%
Oxygen (O_2)	0.03%
Hydrogen Sulfide (H_2S)	0.06 ppmv

Table 4. The Approximate Chemical Compositions of the Gases from the Selected Sampling Sites

Gas Property	Raw Dairy Farm Gas	Raw Landfill Gas	Processed Biomethane
Methane (CH_4)	62%	59.52%	94.38%
Carbon Dioxide (CO_2)	35%	35.22%	1.16%
Nitrogen (N_2)	2%	3.63%	3.13%
Helium (He)	BDL	BDL	BDL
Mercury (Hg)	0.06 $\mu g/m^3$	No Data	BDL
Oxygen (O_2)	0.4%	1.35%	0.53%
Hydrogen Sulfide (H_2S)	4,225 ppmv	28.10 ppmv	BDL

Note: Concentrations are in mol%, unless specified otherwise. Natural Gas quantities are based on LDC tariffs. BDL denotes quantities below the detection limits of the instrumentation used for analysis.

Table 5. Summary of the Test Samples for Natural Gas Saturation Test

Length×Width (inch)	Thickness (inch)	Test	NBR	SBR	PE2708
1×1	0.25	Dimensional Change	NA	NA	6
	0.125		6	6	NA
5.75×2.25	0.25	Hardness	NA	NA	2
	0.125	Hardness & Compression	4	4	NA
2×1.625	0.125	Hardness (Out Gas)	6	6	NA
4.5×0.75	0.125	Tensile	8	8	NA
	0.16		NA	NA	7
1.97×0.98	0.25	Slow Crack Growth	NA	NA	6
0.25×0.25	0.25	Head Space	NA	NA	30
0.5×0.5	0.125		28	28	NA

Table 6. Baseline Test Results

Material Type	Density (g/cm^3)	Hardness (Shore A)	Extractable Mass Loss (Percent)
NBR	1.179	70	3.8
SBR	1.356	68	10.2
MDPE	0.942	Not Complete	N/A

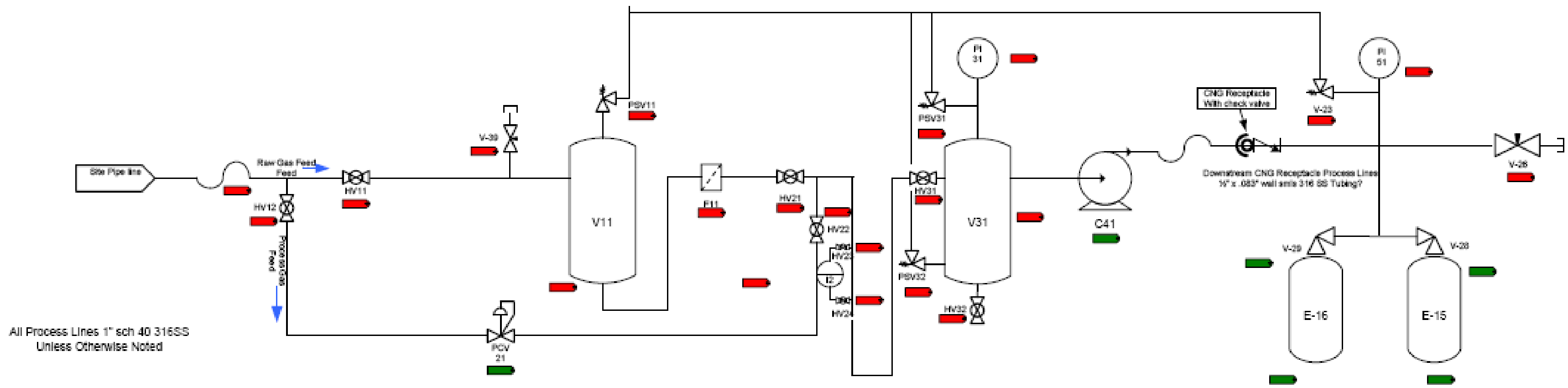


Figure 2. Biogas Collection Schematic (Updated)

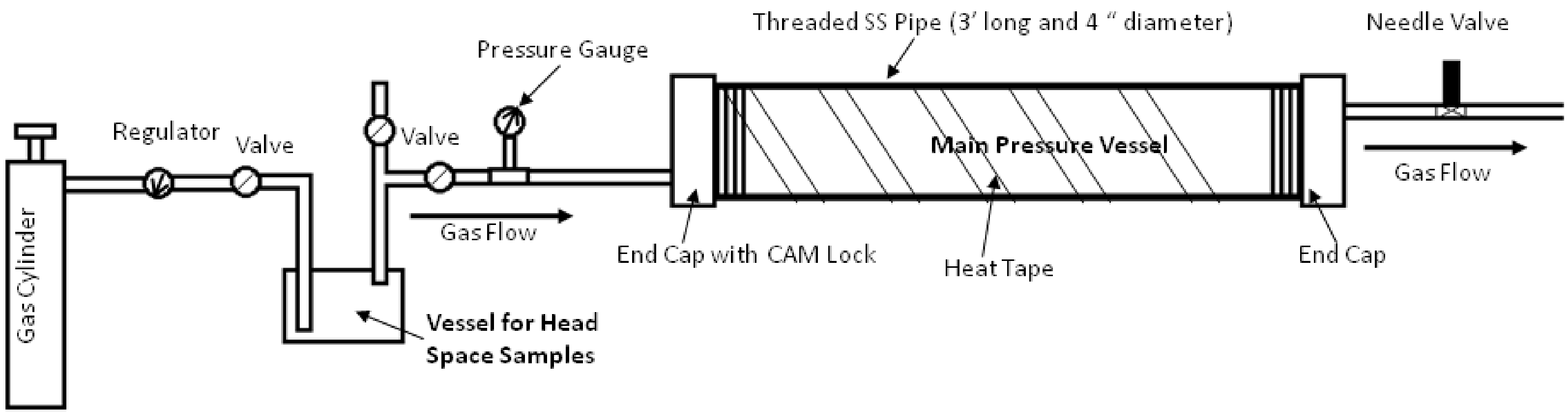
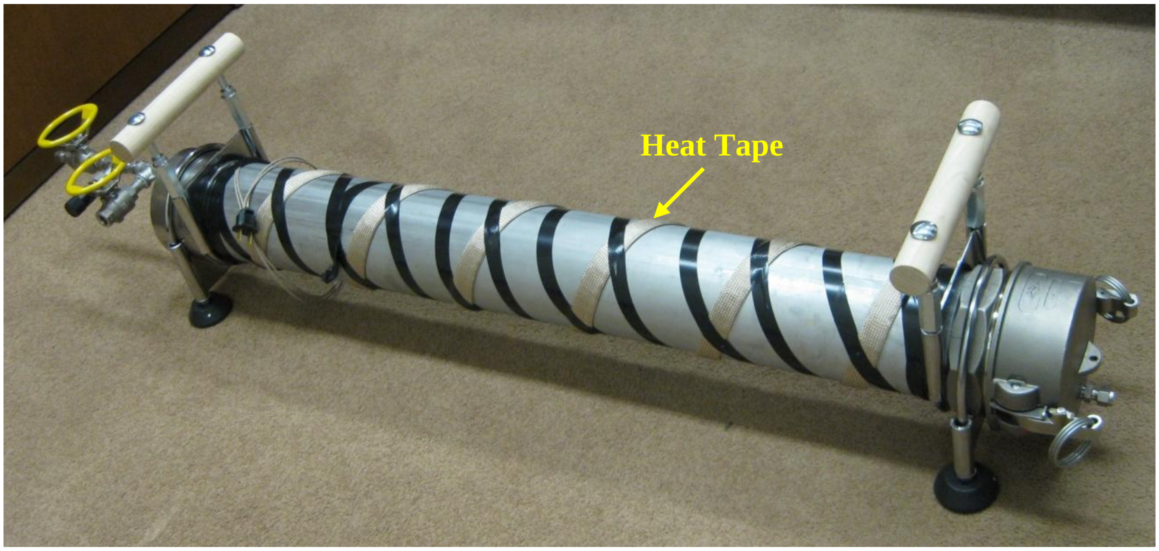


Figure 3. Gas Saturation Test Setup



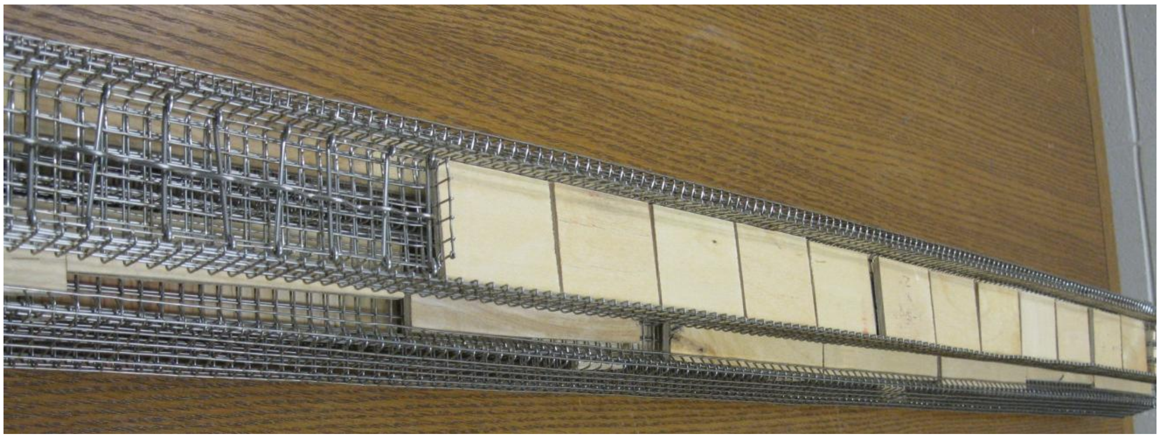


Figure 4. The Main Pressure Vessel and Test Sample Cage

Figure 5. The Pressure Vessel for Head Space Test Samples

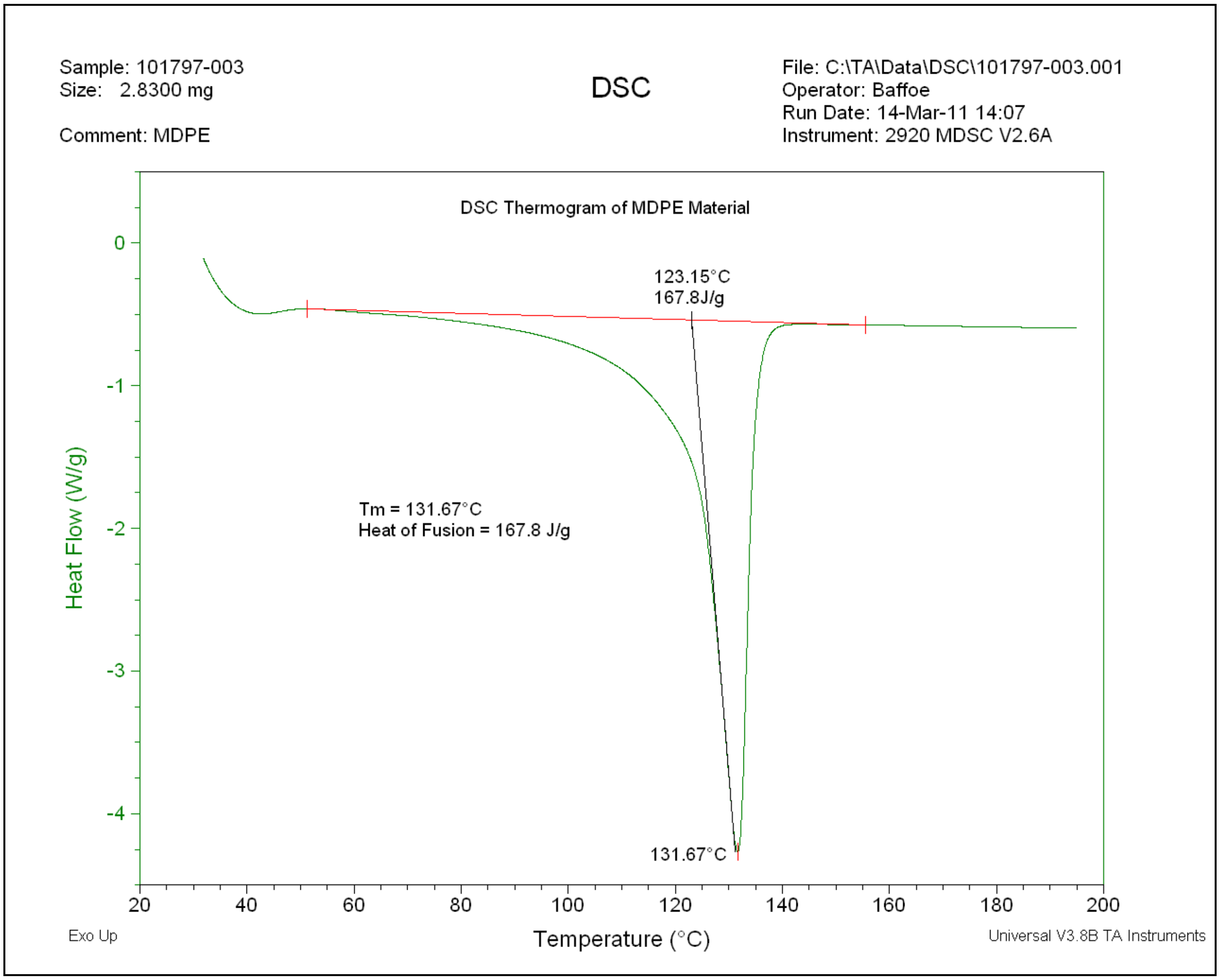


Figure 6. DSC Thermogram of MDPE Material

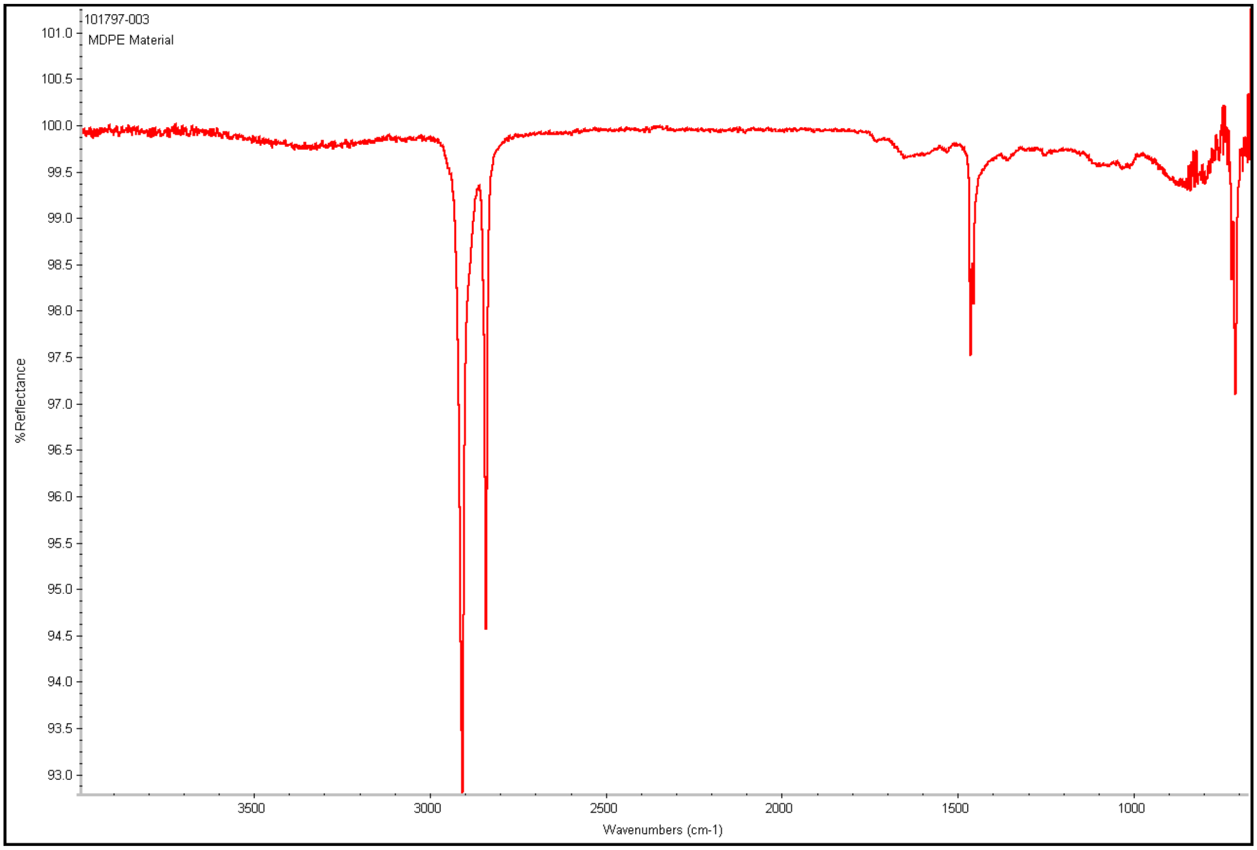


Figure 7. FTIR Thermogram of MDPE Material (by Attenuated Total Reflection Spectroscopy)

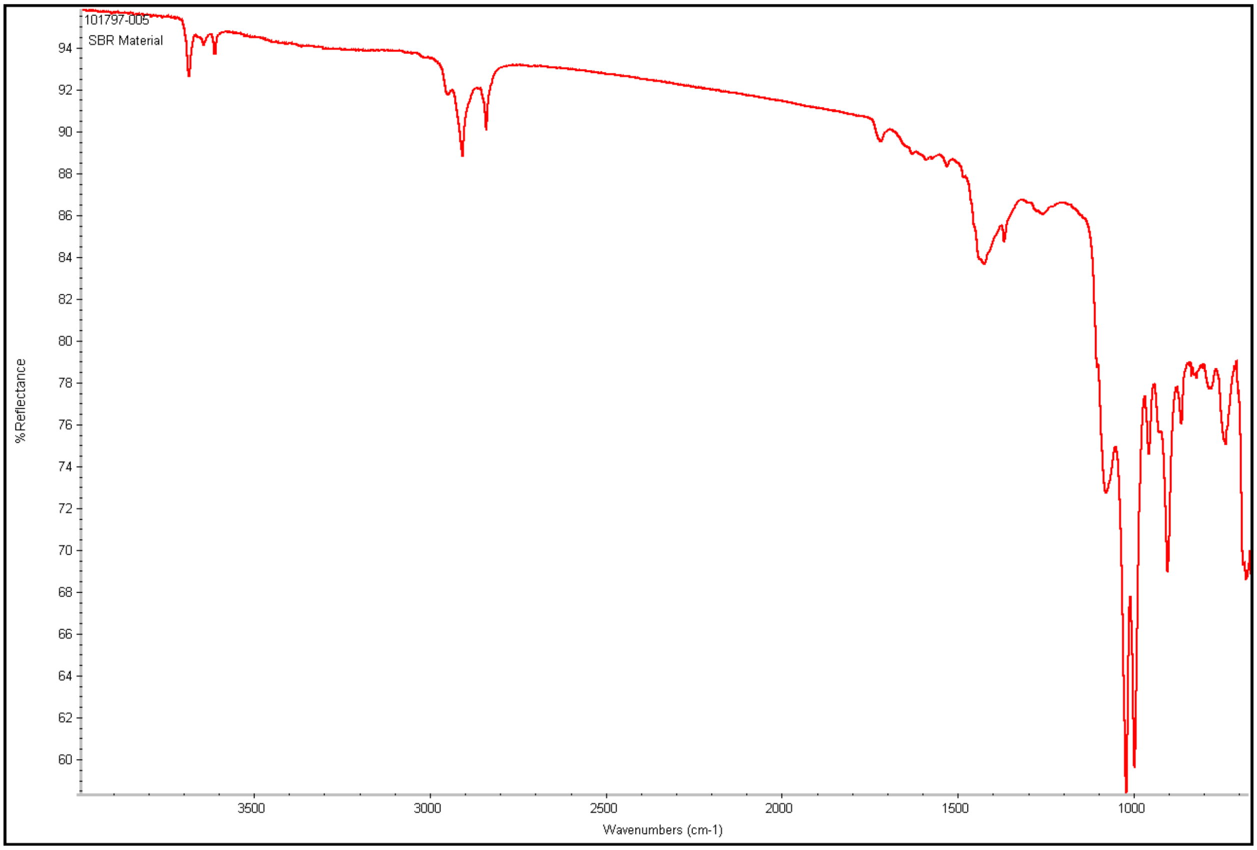


Figure 8. FTIR Thermogram of SBR Material (by Attenuated Total Reflection Spectroscopy)

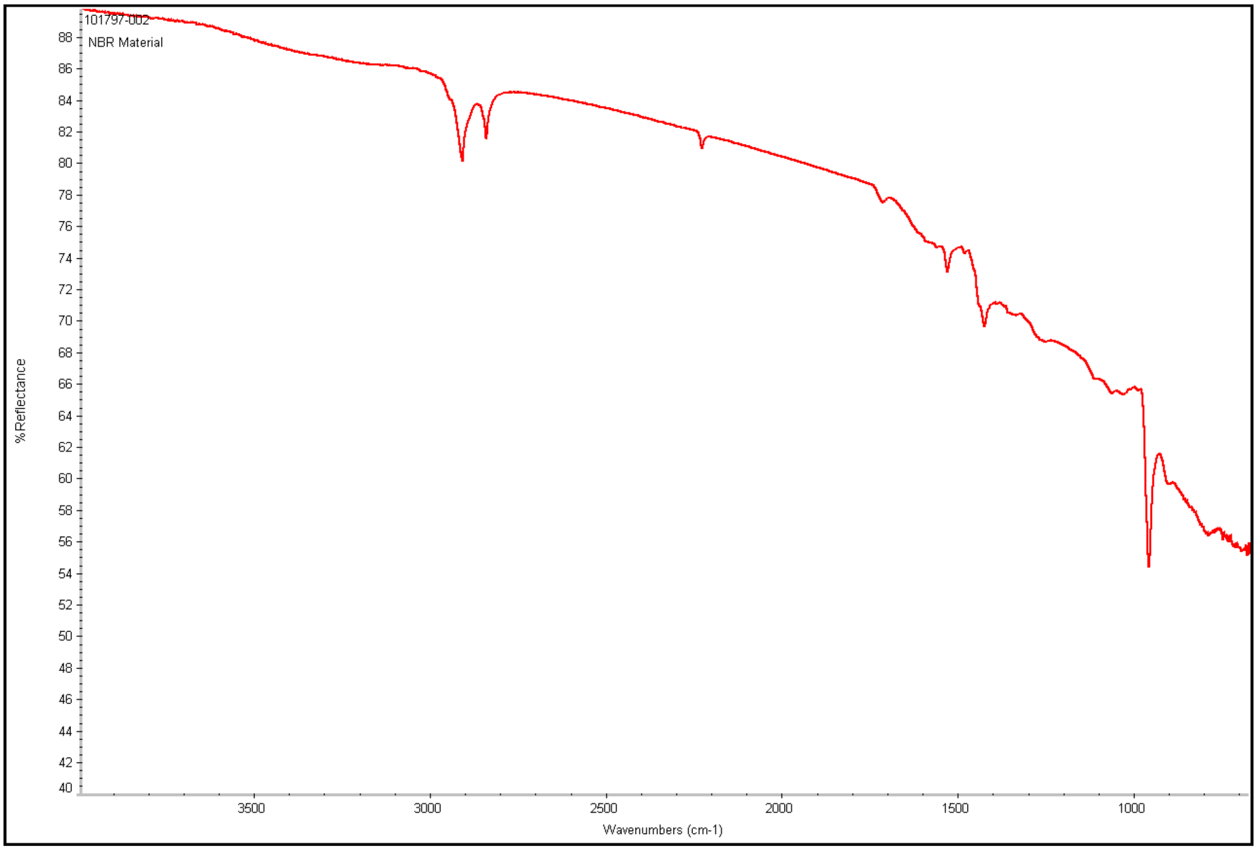


Figure 9. FTIR Thermogram of NBR Material (by Attenuated Total Reflection Spectroscopy)

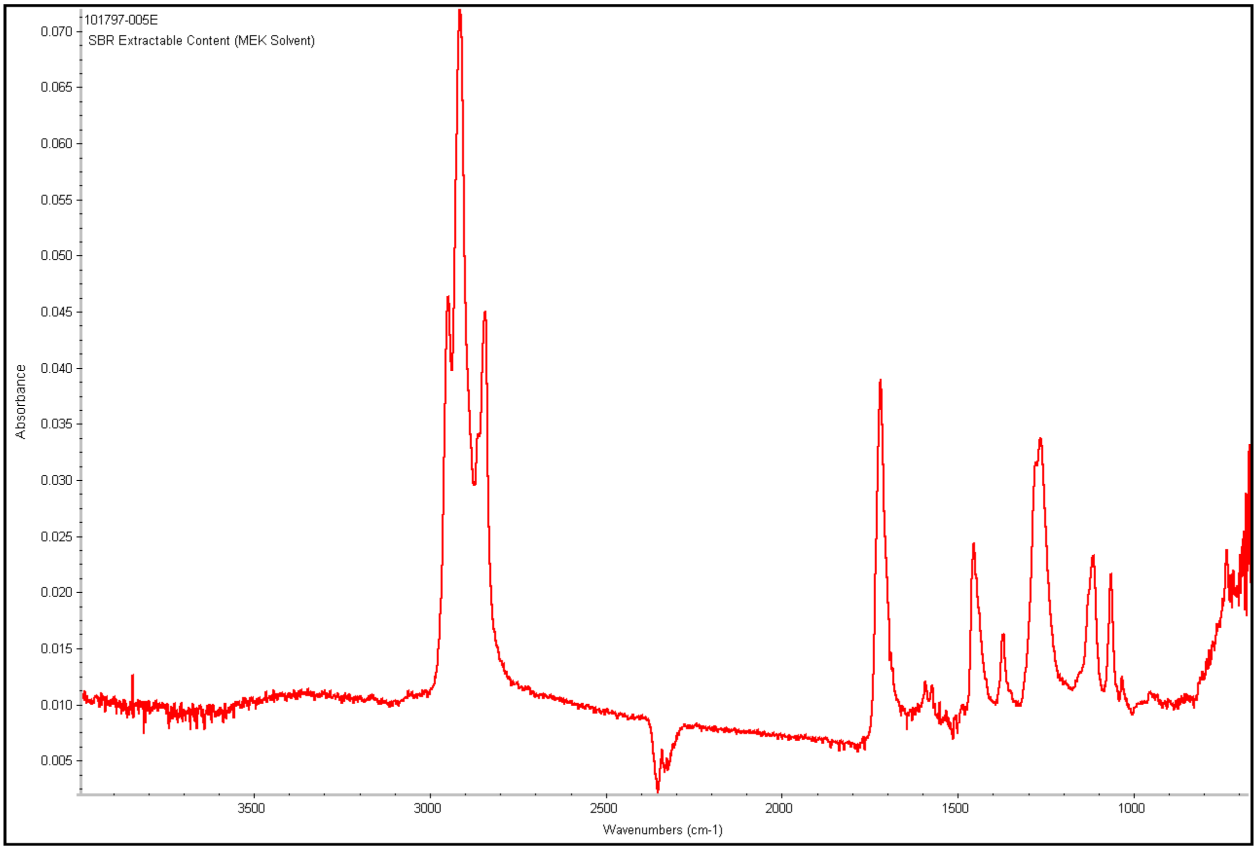


Figure 10. FTIR Thermogram of SBR Extractable Content

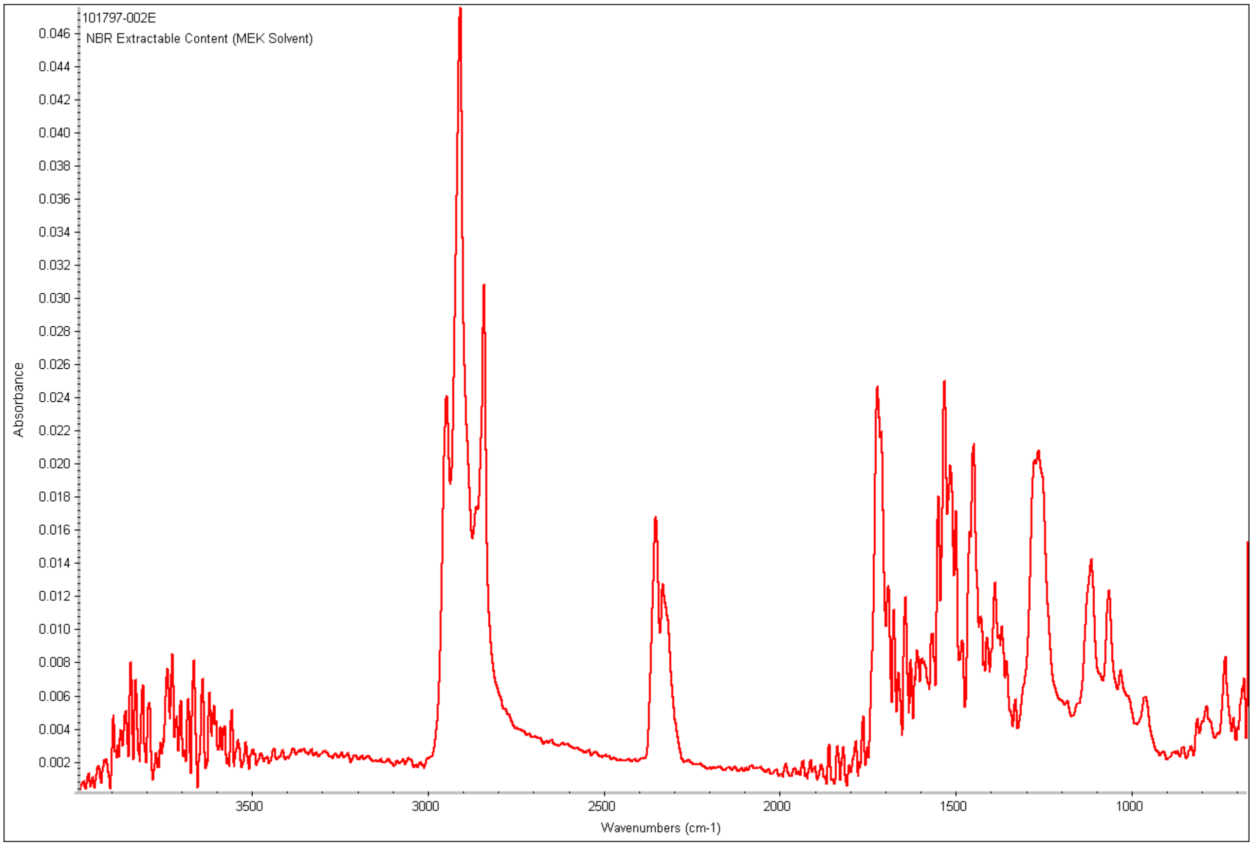


Figure 11. FTIR Thermogram of NBR Extractable Content